

# Surface formation of HCOOH at low temperature

S. Ioppolo,<sup>1</sup> H. M. Cuppen,<sup>1,2</sup> E. F. van Dishoeck<sup>2,3</sup> and H. Linnartz<sup>1</sup>

<sup>1</sup>Raymond & Beverly Sackler Laboratory for Astrophysics, Leiden Observatory, Leiden University, the Netherlands

<sup>2</sup>Leiden Observatory, Leiden University, the Netherlands

<sup>3</sup>Max-Planck-Institut für Extraterrestrische Physik, Giessenbachstrasse 1, Germany

Monthly Notices  
of the

ROYAL ASTRONOMICAL SOCIETY

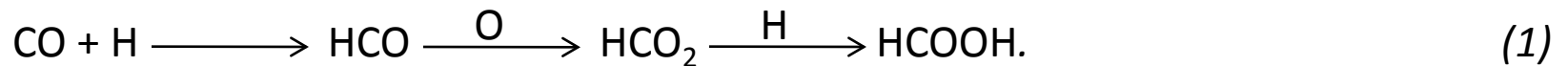


*Mon. Not. R. Astron. Soc.* **2011**, *410*, 1089

Radha Gobinda Bhuiin  
CY10D047  
09-04-11

## Introduction:

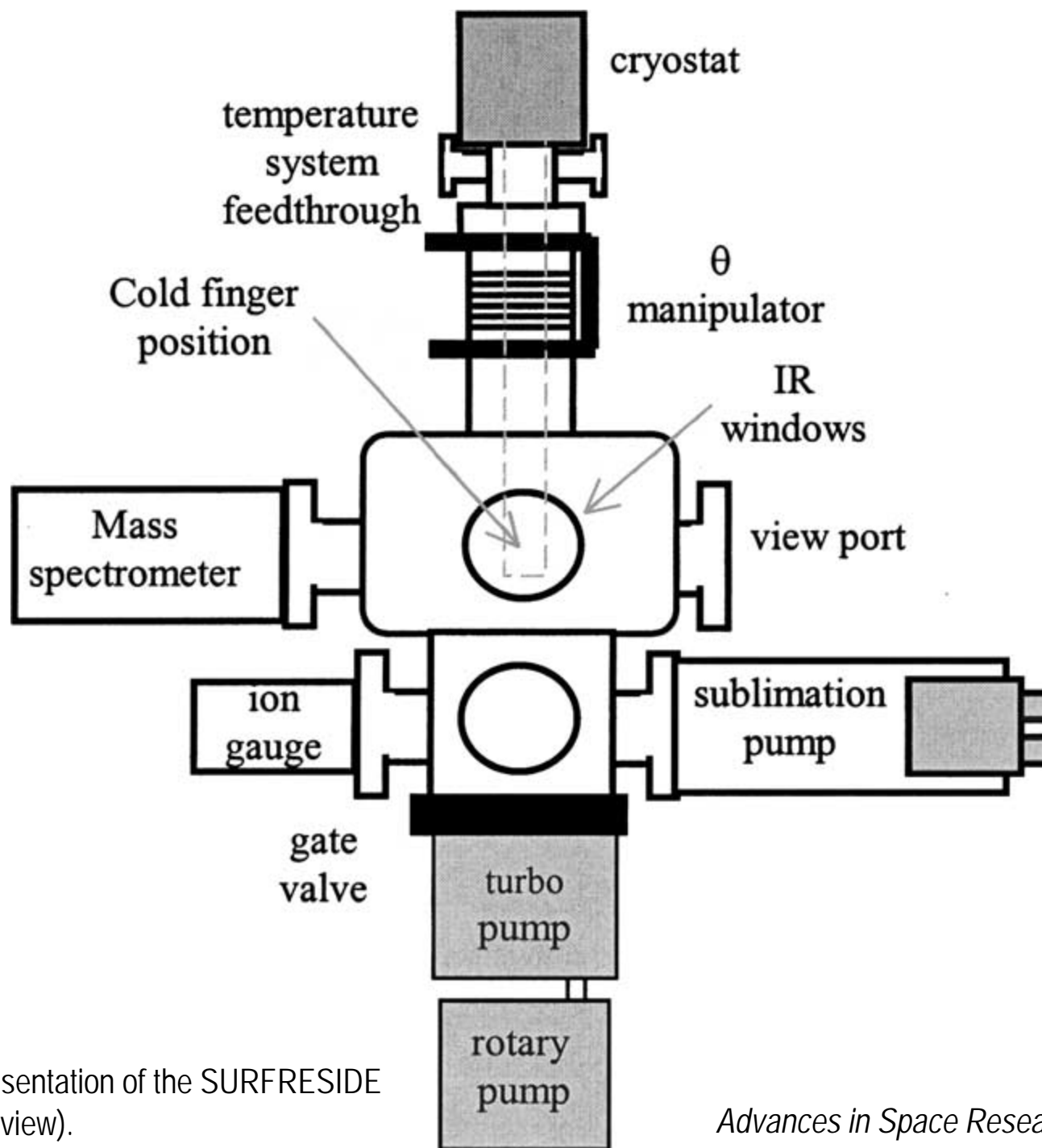
- ❖ The production of formic acid (HCOOH) in cold and hot regions of the interstellar medium is not well understood.
- ❖ Huebner (1984) discussed in their gas-phase model that HCOOH can be formed in dense interstellar clouds through the dissociative recombination of protonated formic acid (HCOOH<sub>2</sub><sup>+</sup>), which forms by radiative association of HCO<sup>+</sup> and H<sub>2</sub>O.
- ❖ According to Vigren *et al.* (2010), who combined a laboratory study and a gas-phase model, dissociative recombination of protonated formic acid is not as efficient as previously thought and the branching ratio of the channel leading to HCOOH has a maximum of only ~ 13 per cent.
- ❖ Therefore, they suggested that HCOOH is predominantly formed in dense interstellar clouds through surface reactions on grains, even though experimental evidence for the efficiency of surface reactions is largely lacking.
- ❖ Several solid-phase reaction channels have been proposed in the past decades.



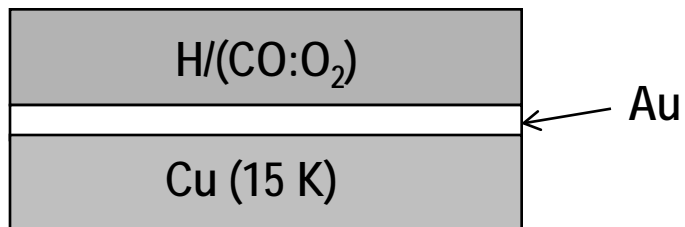
## In this paper:

- ❖ The first experimental evidence for an efficient solid-state reaction scheme providing a way to form HCOOH under astronomical conditions.
- ❖ Several surface reaction channels have been tested under fully controlled experimental conditions by using a state-of-the-art ultrahigh vacuum set-up through co-deposition of H atoms and CO:O<sub>2</sub> mixtures with 4:1, 1:1 and 1:4 ratios.

# Experiment:



A schematic representation of the SURFRESIDE experiment (side view).



CO:O<sub>2</sub> mixtures with a ratio of 4:1, 1:1 and 1:4 are prepared in a high-vacuum glass line.

H<sub>2</sub> molecules are cracked in a capillary pipe surrounded by a tungsten filament, which is heated to 2200 K.

The same H/[CO:O<sub>2</sub>] = 2 ratio is applied to all the H and CO:O<sub>2</sub> co-deposition experiments.

Pure HCOOH and H<sub>2</sub>CO ices and mixtures of H<sub>2</sub>O:HCOOH and H<sub>2</sub>O:H<sub>2</sub>CO (10:1 and 3:1, respectively) are used as control experiments. The HCOOH containing ices are deposited at 30 K, while the H<sub>2</sub>CO containing ices are formed in situ by hydrogenation of several thin layers (1 monolayer (ML) per step) of pure CO ice or H<sub>2</sub>O:CO mixtures at 12 K.

# Formation of solid HCOOH:

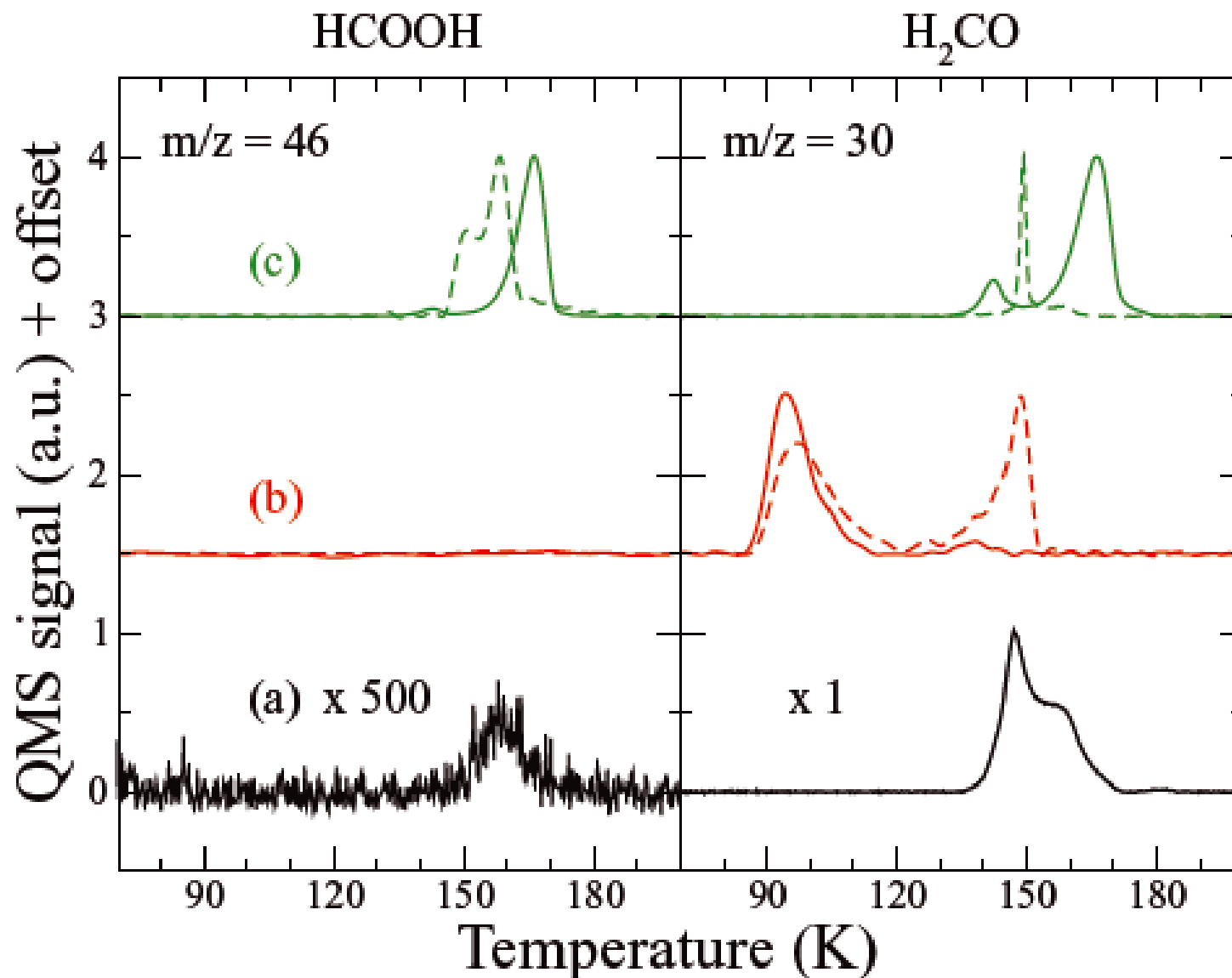


Figure 1. The 46 amu (HCOOH, left - hand column) and 30 amu mass QMS signals (H<sub>2</sub>CO, right - hand column) from the TPD of a H-atom and CO:O<sub>2</sub> = 4:1 co-deposition experiment (a), compared to TPDs of the following experiments: solid H<sub>2</sub>CO (b, solid line), H<sub>2</sub>O:H<sub>2</sub>CO = 3:1 mixture (b, dashed line) and HCOOH ice (c, solid line), H<sub>2</sub>O:HCOOH = 10:1 mixture (c, dashed line). Spectra are offset for clarity.

## Formation temperature:

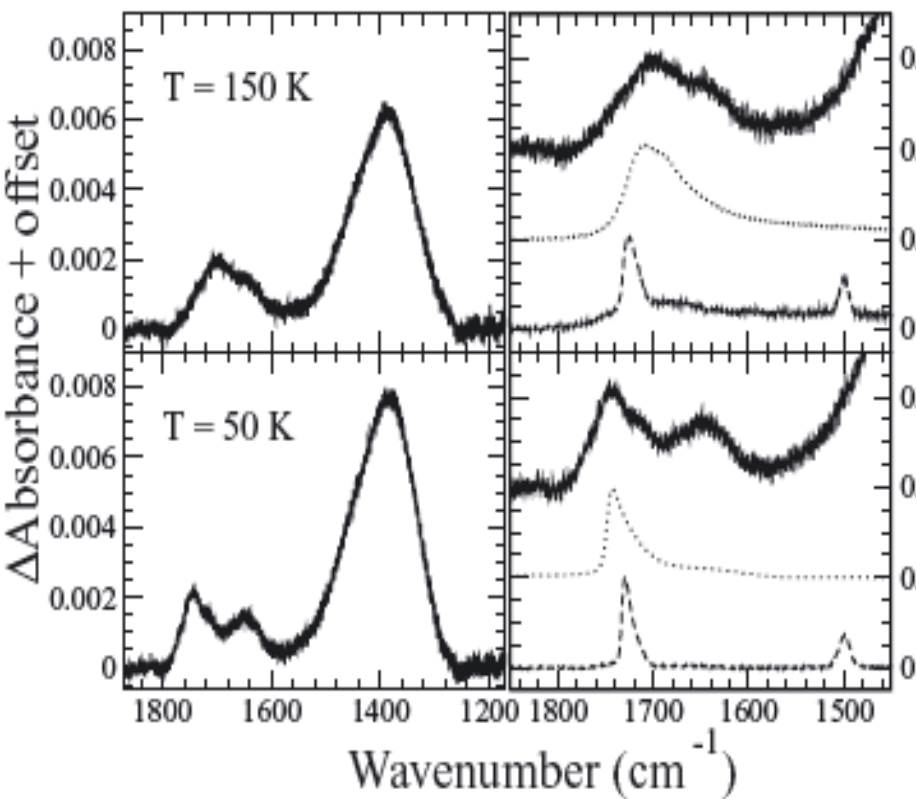


Figure 2. IR spectra from the H-atom and  $\text{CO}:\text{O}_2 = 4:1$  co-deposition experiment (solid lines). The right hand side shows a zoom-in of the  $1700 \text{ cm}^{-1}$  region. For comparison two spectra of mixed  $\text{H}_2\text{O}:\text{HCOOH} = 10:1$  (dotted line) and  $\text{H}_2\text{O}:\text{H}_2\text{CO} = 3:1$  (dashed line) are shown in the top-right panel, and two spectra of pure  $\text{HCOOH}$  (dotted line) and  $\text{H}_2\text{CO}$  (dashed line) are plotted in the bottom-right panel. Spectra are offset for clarity.

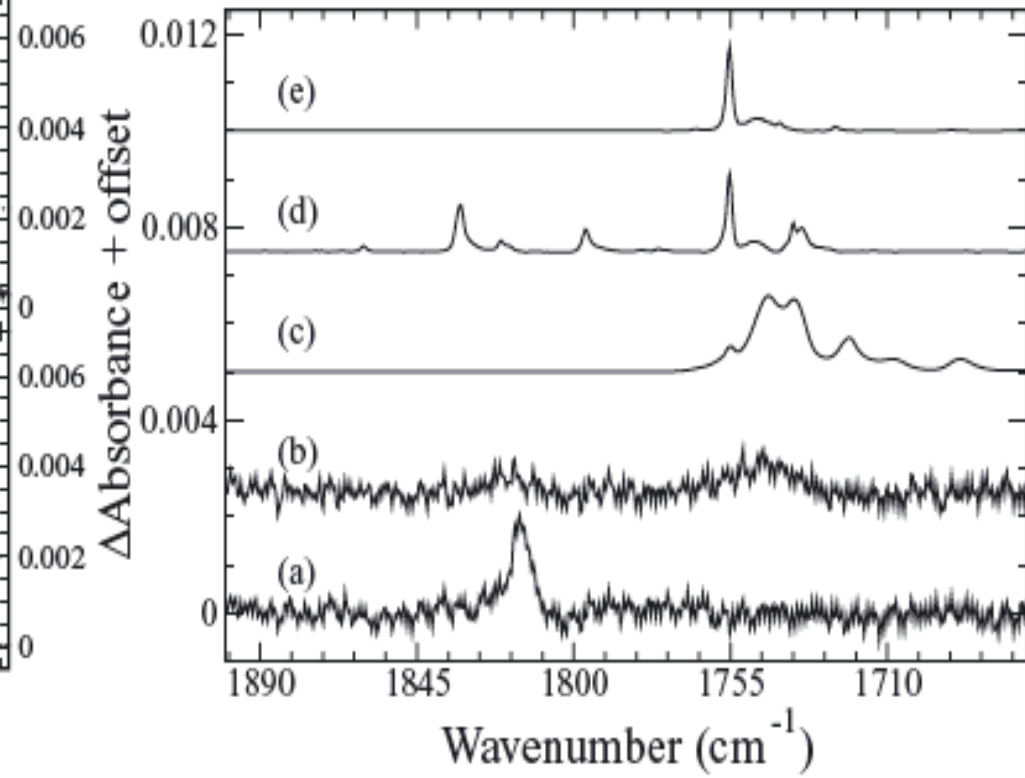


Figure 3. IR spectra from a H-atom and  $\text{CO}:\text{O}_2 = 4:1$  co-deposition experiment at 15 K (a) and 30 K (b) compared to a spectrum of  $\text{CO}:\text{HCOOH} = 100:1$  at 15 K (c),  $\text{CO}:\text{HCOOH} = 1000:1$  at 15 K (d) using higher H-atom flux ( $2 \times 10^{14} \text{ cm}^{-2} \text{ s}^{-1}$ ) and  $\text{CO}:\text{O}_2$  flow ( $1 \times 10^{14} \text{ cm}^{-2} \text{ s}^{-1}$ ). Spectra are offset for clarity.

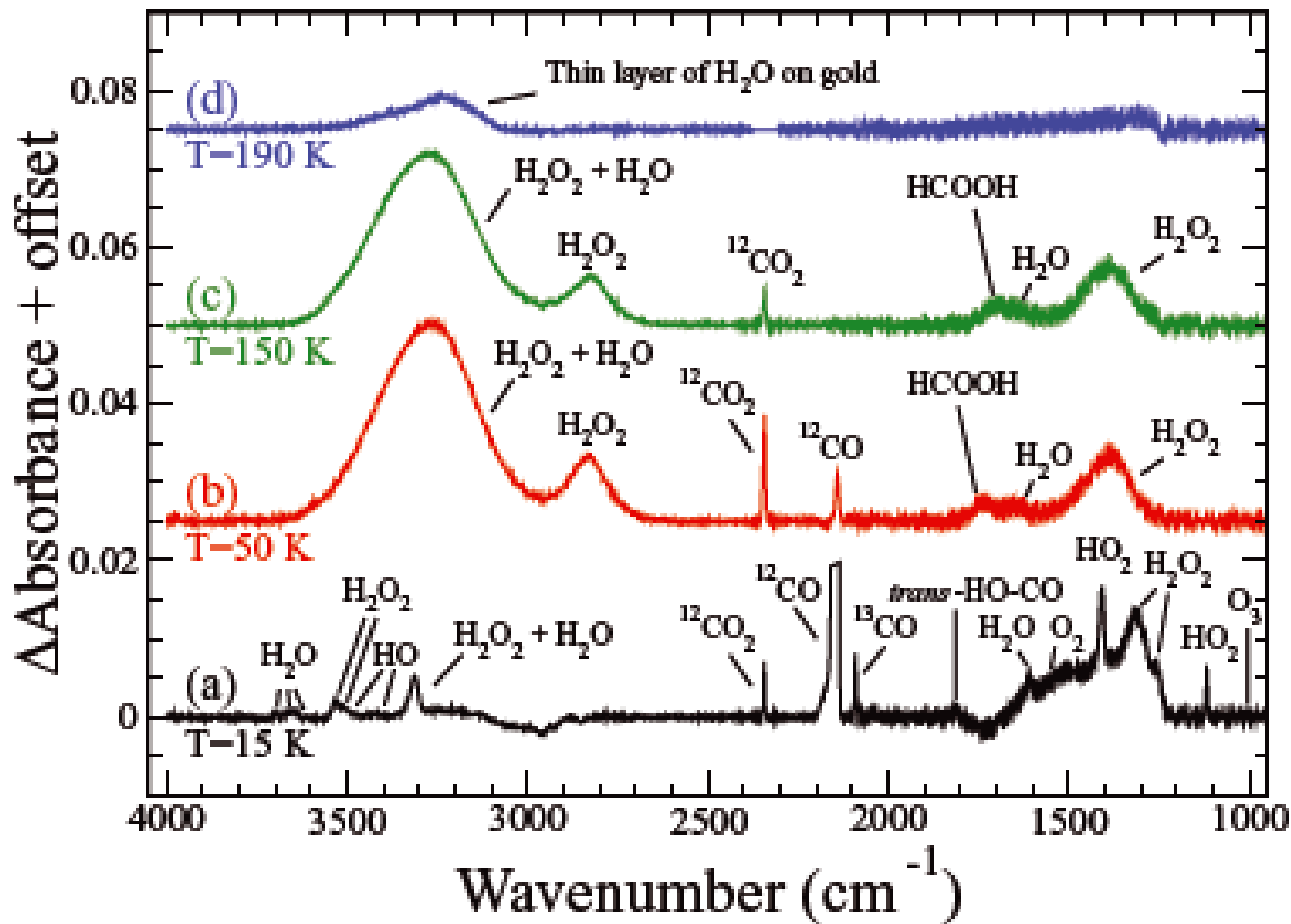
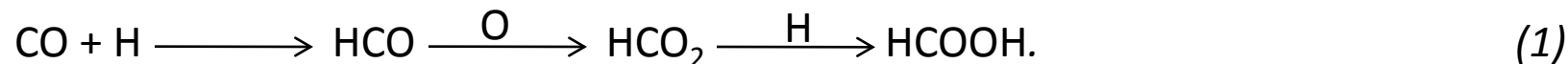


Figure 4. The 15 K (a), 50 K (b), 150 K (c) and 190 K (d) IR spectra of the H-atom and  $\text{CO}:\text{O}_2 = 4:1$  co-deposition experiment after an H-atom fluence of  $2.7 \times 10^{17}$  atoms  $\text{cm}^{-2}$ . Spectra are offset for clarity.



## Possible reaction pathways:

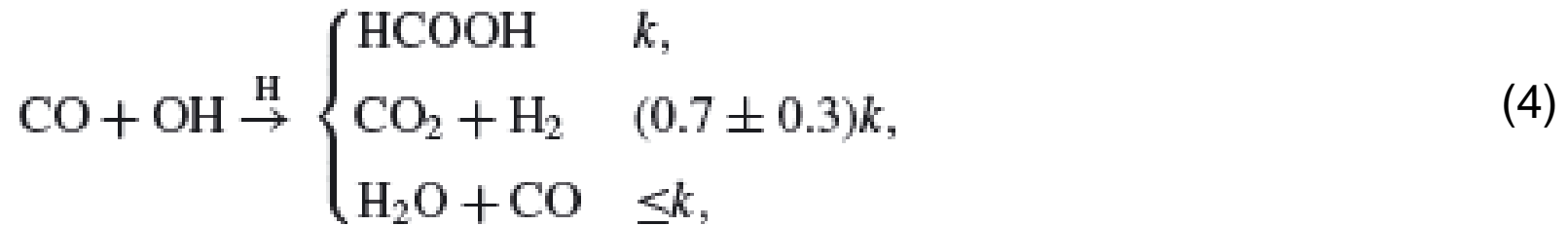
CO ice is not hydrogenated in this experiments, since neither HCO, H<sub>2</sub>CO nor CH<sub>3</sub>OH features appear in the RAIR spectra at 15 K. So, solid HCOOH is therefore most likely formed through reaction (3)



**Table 1.** Assigned IR features with their corresponding reference in the range between 1700 and 1900 cm<sup>-1</sup> as found in a control co-deposition experiment.

Species	Position (cm <sup>-1</sup> )	Reference	Matrix
HCO	1860	Milligan & Jacox (1964)	Ar
<i>trans</i> -HO-CO	1833	Milligan & Jacox (1971)	CO
<i>trans</i> -HO-CO	1820	Zheng & Kaiser (2007)	H <sub>2</sub> O
<i>cis</i> -HO-CO	1796	Milligan & Jacox (1971)	CO
<i>cis</i> -HO-CO	1775	Zheng & Kaiser (2007)	H <sub>2</sub> O
HCOOH	1755	This work	CO
HCOOH	1748	This work	CO
H <sub>2</sub> CO	1737	Nelander (1980)	N <sub>2</sub>
H <sub>2</sub> CO	1734	Nelander (1980)	N <sub>2</sub>

Branching ratio of reaction HO–CO + H:



where  $k$  is the branching ratio of the channel leading to HCOOH.

## Conclusion:

- ❖ Formation of HCOOH is observed at low temperatures mainly through hydrogenation of the HO–CO complex, while reactions with the HCO radical as intermediate are found to be inefficient.
- ❖ The HO–CO complex channel should be considered an important HCOOH formation route, since it could explain the presence of HCOOH in dense molecular clouds.
- ❖ These results are in agreement with density functional theory models, which suggest that there could be equal branching ratio between the three possible channels.

Thank you